

PATENT ABSTRACTS OF JAPAN

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(11)Publication number : 11-073960

(43)Date of publication of application : 16.03.1999

(51)Int.Cl.

H01M 4/58

H01M 4/02

H01M 10/40

(21)Application number : 09-234906

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(22)Date of filing : 29.08.1997

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(54) POSITIVE ELECTRODE ACTIVE MATERIAL FOR NONAQUEOUS ELECTROLYTE SECONDARY BATTERY AND THE NONAQUEOUS ELECTROLYTE SECONDARY BATTERY**(57)Abstract:**

PROBLEM TO BE SOLVED: To provide a positive electrode active material having high energy density at a high working voltage, a long cycle life, and no reduction in discharge capacity at a high temperature by dissolving Mg, Zn and Cr, Co, Fe, Ni or the like to a lithium manganese compound oxide, and baking the mixture in an oxidizing gas.

SOLUTION: As a starting material, an oxide, hydroxide, carbonate, nitrate, or organic acid salt of a metal element constituting the general formula: $\text{Li}_x\text{M}_1\text{yM}_2\text{zMn}_{2-y-z}\text{O}_4$ is used. In the formula, M2 represents one or more elements selected from Cr, Co, Ni, and Fe, M1 represents an element other than M2 except for Mn, such as Mg, Zn or the like which is capable of forming a divalent metal ion, (x), (y), and (z) where $0 < x \leq 1.5$, $0 \leq y \leq 0.5$, $0 \leq z \leq 0.5$, wherein y and z are not 0 at the same time. This starting material is baked at about 600–1000° C in an oxidizing gas having an oxygen concentration of 50% or more for about 10–50 hours. Thus, the elements represented by M1 and M2, Mn and oxygen are firmly bonded to prevent Mn from being dissolved into an electrolyte, even if a voltage is applied at a high temperature.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平11-73960

(43) 公開日 平成11年(1999) 3月16日

(51) Int.Cl.⁶

識別記号

F I

H 0 1 M 4/58

H 0 1 M 4/58

4/02

4/02

C

10/40

10/40

Z

審査請求 未請求 請求項の数 3 O L (全 3 頁)

(21) 出願番号 特願平9-234906

(22) 出願日 平成9年(1997) 8月29日

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(54) 【発明の名称】 非水電解質二次電池用正極活物質及び非水電解質二次電池

(57) 【要約】

【課題】 高い作動電圧でエネルギー密度が高く、サイクル寿命が長く、かつ高温電圧印加による放電容量の低下のない非水二次電池用正極活物質の提供。

【解決手段】 酸素濃度が50%以上の酸化性気体中で焼成された $Li_x M^1 M^2 M_n O_z$ を正極活物質 (M^1 は M^1 以外かつ Mn 以外の元素で2価金属イオンとなりうる元素。 M^2 は Cr 、 Co 、 Ni 又は Fe 。 $0 < x \leq 1.5$ 、 $0 \leq y \leq 0.5$ 、 $0 \leq z \leq 0.5$ 。 $y = z = 0$ ではない。) とする。

【特許請求の範囲】

【請求項1】一般式 $Li, M^1, M^2, Mn_{z-v-z} O_z$ で表される酸化物（ただし、 M^1 はCr、Co、Ni及びFeからなる群から選ばれる1種以上の元素、 M^2 は M^1 以外かつMn以外の元素で2価金属イオンとなりうる1種以上の元素であり、 $0 < x \leq 1.5$ 、 $0 \leq y \leq 0.5$ 、 $0 \leq z \leq 0.5$ であり、 y と z は同時に0ではない。）であり、かつ酸素濃度が50%以上の酸化性気体中で焼成されてなることを特徴とする非水電解質二次電池用正極活物質。

【請求項2】前記一般式において、 M^1 がZn又はMgである請求項1記載の非水電解質二次電池用正極活物質。

【請求項3】リチウム又はリチウムを吸蔵、放出できる物質を負極活物質として有し、請求項1又は2記載の正極活物質を有することを特徴とする非水電解質二次電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、非水電解質二次電池の正極活物質に関する。

【0002】

【従来の技術】リチウム又はリチウムを吸蔵、放出できる化合物を負極とする非水電解質二次電池は、高いエネルギー密度を有するものとして期待され、多くの研究が行われている。近年この電池の正極活物質としてスピネル系リチウムマンガン複合酸化物 ($LiMn_2O_4$) が検討されている。しかし、この正極活物質を用いる場合サイクル特性が不十分で、充放電を繰り返すと放電容量が顕著に低下する問題があった。この原因としては、充放電に伴ってLiイオンが結晶内で移動することにより結晶構造が変形したり部分的破壊が起こるためと考えられる。

【0003】上記の問題点を解決するために、Mnの一部をFe、Co、Cr、Ni等の元素で置換することで結晶格子を安定化させる方法が提案されている。しかし、このような方法で作成した正極活物質を用いて電池を作製しても、高温においては、電圧印加試験を行うと $LiMn_2O_4$ 正極活物質を用いた場合と同様に、Mnが電気化学的に電解液中に溶解し、放電容量が大幅に低下する問題があり、実用化には至っていない。

【0004】

【発明が解決しようとする課題】本発明は、従来技術のこのような問題を解決し、高い作動電圧でエネルギー密度が高く、サイクル寿命が長く、かつ高温で電圧印加しても放電容量の低下のない非水電解質二次電池を得るための正極活物質、及び該正極活物質を有する非水電解質二次電池を提供することを目的とする。

【0005】

【課題を解決するための手段】本発明は、一般式 $Li, M^1, M^2, Mn_{z-v-z} O_z$ で表される酸化物（ただし、 M^1 はCr、Co、Ni及びFeからなる群から選ばれる1種以上の元素、 M^2 は M^1 以外かつMn以外の元素で2価金属イオンとなりうる1種以上の元素であり、 $0 < x \leq 1.5$ 、 $0 \leq y \leq 0.5$ 、 $0 \leq z \leq 0.5$ であり、 y と z は同時に0ではない。）であり、かつ酸素濃度が50%以上の酸化性気体中で焼成されてなることを特徴とする非水電解質二次電池用正極活物質を提供する。

$M^1, M^2, Mn_{z-v-z} O_z$ で表される酸化物（ただし、 M^1 はCr、Co、Ni及びFeからなる群から選ばれる1種以上の元素、 M^2 は M^1 以外かつMn以外の元素で2価金属イオンとなりうる1種以上の元素であり、 $0 < x \leq 1.5$ 、 $0 \leq y \leq 0.5$ 、 $0 \leq z \leq 0.5$ であり、 y と z は同時に0ではない。）であり、かつ酸素濃度が50%以上の酸化性気体中で焼成されてなることを特徴とする非水電解質二次電池用正極活物質を提供する。

【0006】本発明で、一般式 $Li, M^1, M^2, Mn_{z-v-z} O_z$ において M^1 で表される元素は M^2 以外かつMn以外の元素で2価の金属イオンとなりうる元素であり、例えばMg、Zn等が好ましい。リチウムマンガン複合酸化物に M^1 で表される元素が固溶することにより、充放電サイクルの繰り返しによる放電容量の低下がきわめて少なくなり、サイクル特性が向上する。

【0007】 M^1 で表される元素の含有量を表す y の値は $0 \leq y \leq 0.5$ であるが、0.5を超えると $LiMn_2O_4$ のスピネル構造を保てなくなり、放電容量が極端に低下する。より好ましくは $0.1 \leq y \leq 0.3$ である。

【0008】また、 M^2 で表される元素はCr、Co、Fe及びNiからなる群から選ばれる1種以上であるが、 M^2 で表される元素がリチウムマンガン複合酸化物に固溶することにより、Mnの結合状態が安定化し、高温での電圧印加時のMnの電解液への溶解を効果的に防止できる。 M^2 で表される元素の含有量を表す z の値は $0 \leq z \leq 0.5$ であるが、0.5を超えると放電容量が極端に低下する。より好ましくは $0.1 \leq z \leq 0.3$ である。

【0009】本発明の正極活物質を製造するにあたり、出発物質としては一般式 $Li, M^1, M^2, Mn_{z-v-z} O_z$ を構成する金属元素の酸化物、水酸化物、炭酸塩、硝酸塩、有機酸塩等を使用できる。

【0010】本発明の正極活物質は、酸素濃度が50%以上の酸化性気体中で焼成して得られる。酸素濃度は70%以上がより好ましく、90%以上がさらに好ましい。50%以上で焼成すると高温で電圧印加をしても放電容量の低下がきわめて少ない。この理由は明らかではないが、酸素濃度が高い雰囲気中で焼成することにより、一般式 $Li, M^1, M^2, Mn_{z-v-z} O_z$ における M^1 及び M^2 で表される元素及びMnと酸素との結合が強固になり、高温で電圧印加してもMnが電解液中に溶解することを抑制できるためと考えられる。

【0011】また、焼成温度としては600～1000℃が好ましく、特に700～900℃とすることが好ましい。600℃未満であると結晶成長が不十分であり、充放電容量が小さくなる。1000℃を超えると、結晶が成長しすぎ、サイクル特性が劣化する。

【0012】焼成時間は10～50時間が好ましく、特に15～45時間とすることが好ましい。10時間未満

であると結晶成長が不充分であり、充放電容量が小さくなる。50時間を超えると結晶が若干成長しすぎ、サイクル特性が劣化する傾向がある。

【0013】また、合成時の均一化を図るため、適当な焼成時間経過後に一旦焼成炉から取り出し、焼成物を粉碎混合し、再度焼成する工程を採用することが望ましい。そして、焼成終了後適当に徐冷することが好ましい。

【0014】

【実施例】以下に実施例(例1~4)及び比較例(例5、6)により本発明を具体的に説明するが、本発明はこれらに限定されない。

【0015】【例1】 Li_2CO_3 、 MnCO_3 、 Fe_2O_3 及び ZnO をモル比で20:60:50:1となるようにボールミルで混合し、酸素70%窒素30%の雰囲気中で800℃で2時間焼成後、取り出した。この焼成物を粉碎した後、再び同じ雰囲気中で800℃で20時間焼成し、その後24時間かけて室温まで徐冷し、焼成物を乳鉢で粉碎した。これを元素吸光法により分析した結果、 $\text{Li}_{0.9}$ 、 $\text{Fe}_{0.25}$ 、 $\text{Zn}_{0.25}$ 、 $\text{Mn}_{1.5}$ 、 O_4 であった。

【0016】この粉碎物85重量部に導電材としてケッチェンブラックを10重量部と結着剤としてポリフッ化ビニリデン樹脂5重量部を加え、N-メチルピロリドンに溶解させてスラリーとした。このスラリーを厚さ30 μm のアルミニウム箔に均一に塗布して塗膜を形成し、180℃で乾燥させてからローラプレス機にて塗膜の厚さが100 μm になるまで圧延し、その後20mm×20mmの大きさに切断して正極とした。

【0017】次いで厚さ0.6mmの金属リチウム箔を25mm×25mmの大きさに切断し、端部にニッケルリードを圧着したものを作成し、負極とした。負極と正極とをそれぞれの塗布面が向き合うように対向させ、間にセパレータとして厚さ25 μm のポリプロピレン製のマイクロポラスフィルムを介在させ充分な電解液の存在する容器中で、負極端子4、正極端子5に充放電電源を接続し、60℃のアルゴン雰囲気中で電圧印加試験を行った。電解液としては、 LiPF_6 を1mol/lの濃度で炭酸エチレンと炭酸プロピレンとの混合溶媒(体積比で1:1)に溶解した溶液を用いた。

【0018】電圧印加試験の条件としては、充電電圧は

4.3Vまで、放電電圧は3.0Vまで定電流で1mA/cm²の電流密度で充放電を行い初期の放電容量を測定した。再び、4.3Vに充電し、そのまま電圧4.3Vで連続して1ヶ月印加し続けた。その後、3.0Vまで放電して放電容量を測定して、初期値に対する放電容量の維持率を調べたところ、95%であった。

【0019】【例2】正極活物質の焼成雰囲気酸素70%窒素30%とするかわりに酸素100%とした以外は例1と同様にして試料を作製し、例1と同様にして電圧印加試験を行って放電容量の維持率を調べたところ、98%であった。

【0020】【例3】正極活物質の組成を $\text{Li}_{1.0}$ 、 $\text{Fe}_{0.2}$ 、 $\text{Zn}_{0.1}$ 、 $\text{Mn}_{1.7}$ 、 O_4 とした以外は例1と同様にして試料を作製し、例1と同様にして電圧印加試験を行って放電容量の維持率を調べたところ、94%であった。

【0021】【例4】正極活物質の組成を $\text{Li}_{1.0}$ 、 $\text{Co}_{0.1}$ 、 $\text{Zn}_{0.1}$ 、 $\text{Mn}_{1.7}$ 、 O_4 とした以外は例1と同様にして試料を作製し、例1と同様にして電圧印加試験を行って放電容量の維持率を調べたところ、94%であった。

【0022】【例5】正極活物質の焼成雰囲気酸素70%窒素30%とするかわりに空気とした以外は例1と同様にして試料を作製し、例1と同様にして電圧印加試験を行って放電容量の維持率を調べたところ、50%であった。

【0023】【例6】正極活物質の組成を $\text{Li}_{1.0}$ 、 $\text{Mn}_{1.5}$ 、 O_4 とした以外は例1と同様にして試料を作製し、例1と同様にして電圧印加試験を行って放電容量の維持率を調べたところ、3%であった。

【0024】電圧印加試験試験終了後、例5及び例6の電池の負極リチウム上に黒色の堆積物がみられ、例6の場合は特に顕著であった。この堆積物を蛍光X線分析で調べた結果、Mn化合物であることが判明した。これは電圧印加中に正極活物質から溶解したMnイオンが負極リチウム上に析出したものと考えられる。なお例1~4ではMnの堆積物はほとんどみられなかった。

【0025】

【発明の効果】上記実施例及び比較例の結果から明らかに、本発明の正極活物質を有する非水電解質二次電池は、高温における電圧印加による正極活物質の電解液への溶解を防止できるため、容量が維持され、きわめて信頼性が高い。

JAPANESE

[JP,11-073960,A]

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION
TECHNICAL PROBLEM MEANS EXAMPLE

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CLAIMS

[Claim(s)]

[Claim 1] General formula $\text{Li}_x \text{M}_1 \text{yM}_2 \text{zMn}_{2-y-z} \text{O}_4$ The oxide expressed however, one or more sorts of elements chosen from the group which M2 becomes from Cr, Co, nickel, and Fe -- M1 M2 It is one or more sorts of elements which may serve as a divalent metallic ion by elements other than Mn except and, and it is $0 < x \leq 1.5$, $0 \leq y \leq 0.5$, and $0 \leq z \leq 0.5$, and y and z are not 0 simultaneously. it is -- and the positive active material for nonaqueous electrolyte rechargeable batteries to which an oxygen density is calcinated in 50% or more of oxidizing quality gas, and is characterized by the bird clapper

[Claim 2] It sets to the aforementioned general formula and is M1. Positive active material for nonaqueous electrolyte rechargeable batteries according to claim 1 which is Zn or Mg.

[Claim 3] The nonaqueous electrolyte rechargeable battery characterized by having occlusion and the matter which can be emitted for a lithium or a lithium as a negative-electrode active material, and having a positive active material according to claim 1 or 2.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the positive active material of a nonaqueous electrolyte rechargeable battery.

[0002]

[Description of the Prior Art] The nonaqueous electrolyte rechargeable battery which uses a lithium or a lithium occlusion and uses as a negative electrode the compound which can be emitted is expected as what has a high energy density, and many researches are done. The spinel system lithium manganese multiple oxide (LiMn_2O_4) is examined as a positive active material of this cell in recent years. However, when this positive active material was used, the cycle property was inadequate and charge and discharge were repeated, there was a problem to which service capacity falls notably. When Li ion moves within a crystal in connection with charge and discharge as this cause, the crystal structure deforms or it thinks for partial destruction to take place.

[0003] In order to solve the above-mentioned trouble, the method of stabilizing a crystal lattice in replacing a part of Mn by elements, such as Fe, Co, Cr, and nickel, is proposed. However, even if it produces a cell using the positive active material created by such method, when a voltage impression examination is performed in an elevated temperature, it is LiMn_2O_4 . Like the case where a positive active material is used, Mn dissolves in the electrolytic solution electrochemically, there is a problem to which service capacity falls sharply, and it has not resulted in utilization.

[0004]

[Problem(s) to be Solved by the Invention] Even if this invention solves such a problem of the conventional technology, its energy density is high at high operating potential, and its cycle life is long and it carries out voltage impression at an elevated temperature, it aims at offering the nonaqueous electrolyte rechargeable battery which has the positive active material and this positive active material for obtaining a nonaqueous electrolyte rechargeable battery without the fall of service capacity.

[0005]

[Means for Solving the Problem] this invention is general formula $\text{Li}_x\text{M}_1\text{yM}_2\text{zMn}_{2-y-z}\text{O}_4$. The oxide expressed however, one or more sorts of elements chosen from the group which M2 becomes from Cr, Co, nickel, and Fe -- M1 -- M2 It is one or more sorts of elements which may serve as a divalent metallic ion by elements other than Mn except and, and it is $0 < x \leq 1.5$, $0 < y \leq 0.5$, and $0 < z \leq 0.5$, and y and z are not 0 simultaneously. it is -- and the positive active material for nonaqueous electrolyte rechargeable batteries to which an oxygen density is calcinated in 50% or more of oxidizing quality gas, and is characterized by the bird clapper is offered

[0006] At this invention, it is general formula $\text{Li}_x\text{M}_1\text{yM}_2\text{zMn}_{2-y-z}\text{O}_4$. It sets and is M1. The element expressed is M2. It is the element which may serve as a metal ion divalent by elements other than Mn except and, for example, Mg, Zn, etc. are desirable. It is M1 to a lithium manganese multiple oxide. When the element expressed dissolves, the fall of the service capacity by the repeat of a charge-and-discharge cycle decreases extremely, and a cycle property improves.

[0007] M1 The value of y showing the content of an element expressed is LiMn_2O_4 , when 0.5 is exceeded, although it is $0 < y \leq 0.5$. It becomes impossible to maintain Spinel structure and service capacity falls extremely. It is $0.01 \leq y \leq 0.3$ more preferably.

[0008] Moreover, M2 The element expressed is M2 although it is one or more sorts chosen from the group which consists of Cr, Co, Fe, and nickel. When the element expressed dissolves to a lithium manganese multiple oxide, the integrated state of Mn is stable and the dissolution to the electrolytic solution of Mn at the time of the voltage impression in an elevated temperature can be prevented effectively. M2 Although the value of z showing the content of an element expressed is $0 < z \leq 0.5$, if 0.5 is exceeded, service capacity will fall extremely. It is $0.1 \leq z \leq 0.3$ more preferably.

[0009] It is in charge of manufacturing the positive active material of this invention, and is general formula Li_x

M₁yM₂zMn_{2-y-z}O₄ as a starting material. The oxide of the metallic element to constitute, a hydroxide, a carbonate, a nitrate, organic acid chloride, etc. can be used.

[0010] An oxygen density calcinates the positive active material of this invention in 50% or more of oxidizing quality gas, and it is obtained. 70% or more of an oxygen density is more desirable, and is still more desirable.

[90% or more of] If it calcinates at 50% or more, even if it will carry out voltage impression at an elevated temperature, there are very few falls of service capacity. This reason is general formula Lix M₁yM₂zMn_{2-y-z}O₄, when an oxygen density calcinates in a high atmosphere, although it is not clear. M₁ which can be set And M₂ Even if combination with an element, and Mn and oxygen which are expressed becomes firm and carries out voltage impression at an elevated temperature, it thinks because it can suppress that Mn dissolves in the electrolytic solution.

[0011] Moreover, as a burning temperature, 600-1000 degrees C is desirable, and it is desirable to consider as 700-900 degrees C especially. A crystal growth is inadequate in it being less than 600 degrees C, and charge-and-discharge capacity becomes small. If it exceeds 1000 degrees C, a crystal will grow too much and a cycle property will deteriorate.

[0012] 10 - 50 hours of a firing time are desirable, and it is desirable to consider as 15 - 45 hours especially. A crystal growth is inadequate in it being less than 10 hours, and charge-and-discharge capacity becomes small. If it exceeds 50 hours, a crystal will grow too much a little, and there is an inclination for a cycle property to deteriorate.

[0013] Moreover, in order to attain equalization at the time of composition, it is desirable to adopt the process which once takes out from a firing furnace after suitable firing-time progress, carries out pulverization mixture of the baking object, and is calcinated again. And cooling slowly suitably after a baking end is desirable.

[0014]

[Example] Although an example (Examples 1-4) and the example of comparison (Examples 5 and 6) explain this invention concretely below, this invention is not limited to these.

[0015] [Example 1] Li₂CO₃, MnCO₃, and Fe₂O₃ And ZnO was mixed with the ball mill so that it might be set to 20:60:50:1 by the mole ratio, and it took out after 2-hour baking at 800 degrees C in 70% atmosphere of 30% of nitrogen of oxygen. After grinding this baking object, in the again same atmosphere, it calcinated for 20 hours, and ****(ed) to the room temperature over 24 hours after that by 800 degrees C, and the mortar ground the baking object. the result which analyzed this by the element extinction method -- Li_{0.97}Fe_{0.25}Zn_{0.25}Mn_{1.5}O₄ it was .

[0016] Added KETCHIEN black as electric conduction material, added the polyvinylidene-fluoride resin 5 weight section to this pulverization object 85 weight section as 10 weight sections and a binder, and it was made to dissolve in N-methyl pyrrolidone, and considered as the slurry. This slurry was uniformly applied to the aluminum foil with a thickness of 30 micrometers, and the paint film was formed, it rolled out after making it dry at 180 degrees C until the thickness of a paint film was set to 100 micrometers with the roller-press machine, and it cut in the after that 20mmx20mm size, and considered as the positive electrode.

[0017] Subsequently, the metal lithium foil with a thickness of 0.6mm was cut in the 25mmx25mm size, what stuck the nickel lead to the edge by pressure was created, and it considered as the negative electrode. The negative electrode and the positive electrode were made to counter so that each application side may face each other, the charge-and-discharge power supply was connected to the negative-electrode terminal 4 and the positive-electrode terminal 5 in the container with which the micro porous film with a thickness of 25 micrometers made from polypropylene is made to intervene as separator in between, and sufficient electrolytic solution exists in it, and the voltage impression examination was performed in 60-degree C argon atmosphere. As the electrolytic solution, it is LiPF₆. The solution which dissolved in the mixed solvent (it is 1:1 at a volume ratio) of an ethylene carbonate and a propylene carbonate by the concentration of 1 mol/l. was used.

[0018] For charge voltage, as conditions for a voltage impression examination, discharge voltage is 1 mA/cm² at a constant current to 3.0V to 4.3V. Charge and discharge were performed with current density, and early service capacity was measured. Again, 4.3V are charged and it continued impressing for one month continuously by voltage 4.3V as it is. Then, it was 95%, when it discharged to 3.0V, service capacity was measured and the maintenance factor of the service capacity to initial value was investigated.

[0019] [Example 2] Instead of using the firing environments of a positive active material as 30% of 70% nitrogen of oxygen, except having considered as 100% of oxygen, when the sample was produced like Example 1, the voltage impression examination was performed like Example 1 and the maintenance factor of service capacity was investigated, it was 98%.

[0020] [Example 3] composition of a positive active material -- Li_{1.0}Fe_{0.2}Zn_{0.1}Mn_{1.7}O₄ ** -- except having carried out, when the sample was produced like Example 1, the voltage impression examination was performed like Example 1 and the maintenance factor of service capacity was investigated, it was 94%

[0021] [Example 4] composition of a positive active material -- Li_{1.0}Co_{0.2}Zn_{0.1}Mn_{1.7}O₄ ** -- except having carried out, when the sample was produced like Example 1, the voltage impression examination was performed like

Example 1 and the maintenance factor of service capacity was investigated, it was 94%

[0022] [Example 5] Instead of using the firing environments of a positive active material as 30% of 70% nitrogen of oxygen, except having considered as air, when the sample was produced like Example 1, the voltage impression examination was performed like Example 1 and the maintenance factor of service capacity was investigated, it was 50%.

[0023] [Example 6] composition of a positive active material -- $\text{Li}_{1.0} \text{Mn}_{2.0} \text{O}_4$ ** -- except having carried out, when the sample was produced like Example 1, the voltage impression examination was performed like Example 1 and the maintenance factor of service capacity was investigated, it was 3%

[0024] The black sediment on the negative-electrode lithium of the cell of Example 5 and Example 6 was seen after the voltage impression test test end, and it was remarkable especially when it was Example 6. As a result of investigating this sediment by X-ray fluorescence, it became clear that it is Mn compound. This is considered that Mn ion which dissolved from the positive active material during voltage impression deposited on the negative-electrode lithium. In addition, most sediments of Mn were not seen in Examples 1-4.

[0025]
[Effect of the Invention] Since the nonaqueous electrolyte rechargeable battery which has the positive active material of this invention can prevent the dissolution to the electrolytic solution of the positive active material by hot voltage impression, capacity is maintained and it is very reliable, so that clearly from the result of the above-mentioned example and the example of comparison.

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PRIOR ART

[Description of the Prior Art] The nonaqueous electrolyte rechargeable battery which uses a lithium or a lithium occlusion and uses as a negative electrode the compound which can be emitted is expected as what has a high energy density, and many researches are done. The spinel system lithium manganese multiple oxide (LiMn_2O_4) is examined as a positive active material of this cell in recent years. However, when this positive active material was used, the cycle property was inadequate and charge and discharge were repeated, there was a problem to which service capacity falls notably. When Li ion moves within a crystal in connection with charge and discharge as this cause, the crystal structure deforms or it thinks for partial destruction to take place.

[0003] In order to solve the above-mentioned trouble, the method of stabilizing a crystal lattice in replacing a part of Mn by elements, such as Fe, Co, Cr, and nickel, is proposed. However, even if it produces a cell using the positive active material created by such method, when a voltage impression examination is performed in an elevated temperature, it is LiMn_2O_4 . Like the case where a positive active material is used, Mn dissolves in the electrolytic solution electrochemically, there is a problem to which service capacity falls sharply, and it has not resulted in utilization.

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EFFECT OF THE INVENTION

[Effect of the Invention] Since the nonaqueous electrolyte rechargeable battery which has the positive active material of this invention can prevent the dissolution to the electrolytic solution of the positive active material by hot voltage impression, capacity is maintained and it is very reliable, so that clearly from the result of the above-mentioned example and the example of comparison.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Even if this invention solves such a problem of the conventional technology, its energy density is high at high operating potential, and its cycle life is long and it carries out voltage impression at an elevated temperature, it aims at offering the nonaqueous electrolyte rechargeable battery which has the positive active material and this positive active material for obtaining a nonaqueous electrolyte rechargeable battery without the fall of service capacity.

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MEANS

[Means for Solving the Problem] this invention is general formula $\text{Li}_x \text{M}_1 \text{yM}_2 \text{zMn}_{2-y-z} \text{O}_4$. The oxide expressed however, one or more sorts of elements chosen from the group which M2 becomes from Cr, Co, nickel, and Fe -- M1 -- M2 It is one or more sorts of elements which may serve as a divalent metallic ion by elements other than Mn except and, and it is $0 < x \leq 1.5$, $0 \leq y \leq 0.5$, and $0 \leq z \leq 0.5$, and y and z are not 0 simultaneously. it is -- and the positive active material for nonaqueous electrolyte rechargeable batteries to which an oxygen density is calcinated in 50% or more of oxidizing quality gas, and is characterized by the bird clapper is offered

[0006] At this invention, it is general formula $\text{Li}_x \text{M}_1 \text{yM}_2 \text{zMn}_{2-y-z} \text{O}_4$. It sets and is M1. The element expressed is M2. It is the element which may serve as a metal ion divalent by elements other than Mn except and, for example, Mg, Zn, etc. are desirable. It is M1 to a lithium manganese multiple oxide. When the element expressed dissolves, the fall of the service capacity by the repeat of a charge-and-discharge cycle decreases extremely, and a cycle property improves.

[0007] M1 The value of y showing the content of an element expressed is $\text{LiMn}_2 \text{O}_4$, when 0.5 is exceeded, although it is $0 \leq y \leq 0.5$. It becomes impossible to maintain Spinel structure and service capacity falls extremely. It is $0.01 \leq y \leq 0.3$ more preferably.

[0008] Moreover, M2 The element expressed is M2 although it is one or more sorts chosen from the group which consists of Cr, Co, Fe, and nickel. When the element expressed dissolves to a lithium manganese multiple oxide, the integrated state of Mn is stable and the dissolution to the electrolytic solution of Mn at the time of the voltage impression in an elevated temperature can be prevented effectively. M2 Although the value of z showing the content of an element expressed is $0 \leq z \leq 0.5$, if 0.5 is exceeded, service capacity will fall extremely. It is $0.1 \leq z \leq 0.3$ more preferably.

[0009] It is in charge of manufacturing the positive active material of this invention, and is general formula $\text{Li}_x \text{M}_1 \text{yM}_2 \text{zMn}_{2-y-z} \text{O}_4$ as a starting material. The oxide of the metallic element to constitute, a hydroxide, a carbonate, a nitrate, organic acid chloride, etc. can be used.

[0010] An oxygen density calcinates the positive active material of this invention in 50% or more of oxidizing quality gas, and it is obtained. 70% or more of an oxygen density is more desirable, and is still more desirable.

[90% or more of] If it calcinates at 50% or more, even if it will carry out voltage impression at an elevated temperature, there are very few falls of service capacity. This reason is general formula $\text{Li}_x \text{M}_1 \text{yM}_2 \text{zMn}_{2-y-z} \text{O}_4$, when an oxygen density calcinates in a high atmosphere, although it is not clear. M1 which can be set And M2 Even if combination with an element, and Mn and oxygen which are expressed becomes firm and carries out voltage impression at an elevated temperature, it thinks because it can suppress that Mn dissolves in the electrolytic solution.

[0011] Moreover, as a burning temperature, 600-1000 degrees C is desirable, and it is desirable to consider as 700-900 degrees C especially. A crystal growth is inadequate in it being less than 600 degrees C, and charge-and-discharge capacity becomes small. If it exceeds 1000 degrees C, a crystal will grow too much and a cycle property will deteriorate.

[0012] 10 - 50 hours of a firing time are desirable, and it is desirable to consider as 15 - 45 hours especially. A crystal growth is inadequate in it being less than 10 hours, and charge-and-discharge capacity becomes small. If it exceeds 50 hours, a crystal will grow too much a little, and there is an inclination for a cycle property to deteriorate.

[0013] Moreover, in order to attain equalization at the time of composition, it is desirable to adopt the process which once takes out from a firing furnace after suitable firing-time progress, carries out pulverization mixture of the baking object, and is calcinated again. And cooling slowly suitably after a baking end is desirable.

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EXAMPLE

[Example] Although an example (Examples 1-4) and the example of comparison (Examples 5 and 6) explain this invention concretely below, this invention is not limited to these.

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[0016] Added KETCHIEN black as electric conduction material, added the polyvinylidene-fluoride resin 5 weight section to this trituration object 85 weight section as 10 weight sections and a binder, and it was made to dissolve in N-methyl pyrrolidone, and considered as the slurry. This slurry was uniformly applied to the aluminum foil with a thickness of 30 micrometers, and the paint film was formed, it rolled out after making it dry at 180 degrees C until the thickness of a paint film was set to 100 micrometers with the roller-press machine, and it cut in the after that 20mmx20mm size, and considered as the positive electrode.

[0017] Subsequently, the metal lithium foil with a thickness of 0.6mm was cut in the 25mmx25mm size, what stuck the nickel lead to the edge by pressure was created, and it considered as the negative electrode. The negative electrode and the positive electrode were made to counter so that each application side may face each other, the charge-and-discharge power supply was connected to the negative-electrode terminal 4 and the positive-electrode terminal 5 in the container with which the micro porous film with a thickness of 25 micrometers made from polypropylene is made to intervene as separator in between, and sufficient electrolytic solution exists in it, and the voltage impression examination was performed in 60-degree C argon atmosphere. As the electrolytic solution, it is LiPF_6 . The solution which dissolved in the mixed solvent (it is 1:1 at a volume ratio) of an ethylene carbonate and a propylene carbonate by the concentration of 1 mol/l. was used.

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[0019] [Example 2] Instead of using the firing environments of a positive active material as 30% of 70% nitrogen of oxygen, except having considered as 100% of oxygen, when the sample was produced like Example 1, the voltage impression examination was performed like Example 1 and the maintenance factor of service capacity was investigated, it was 98%.

[0020] [Example 3] composition of a positive active material -- $\text{Li}_{1.0}\text{Fe}_{0.2}\text{Zn}_{0.1}\text{Mn}_{1.7}\text{O}_4$ ** -- except having carried out, when the sample was produced like Example 1, the voltage impression examination was performed like Example 1 and the maintenance factor of service capacity was investigated, it was 94%

[0021] [Example 4] composition of a positive active material -- $\text{Li}_{1.0}\text{Co}_{0.2}\text{Zn}_{0.1}\text{Mn}_{1.7}\text{O}_4$ ** -- except having carried out, when the sample was produced like Example 1, the voltage impression examination was performed like Example 1 and the maintenance factor of service capacity was investigated, it was 94%

[0022] [Example 5] Instead of using the firing environments of a positive active material as 30% of 70% nitrogen of oxygen, except having considered as air, when the sample was produced like Example 1, the voltage impression examination was performed like Example 1 and the maintenance factor of service capacity was investigated, it was 50%.

[0023] [Example 6] composition of a positive active material -- $\text{Li}_{1.0}\text{Mn}_{2.0}\text{O}_4$ ** -- except having carried out, when the sample was produced like Example 1, the voltage impression examination was performed like Example 1 and the maintenance factor of service capacity was investigated, it was 3%

[0024] The black sediment on the negative-electrode lithium of the cell of Example 5 and Example 6 was seen after the voltage impression test test end, and it was remarkable especially when it was Example 6. As a result of

investigating this sediment by X-ray fluorescence, it became clear that it is Mn compound. This is considered that Mn ion which dissolved from the positive active material during voltage impression deposited on the negative-electrode lithium. In addition, most sediments of Mn were not seen in Examples 1-4.

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